

## Articles

### Synthesis and Characterization of the Platinum Cluster Complex Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub>

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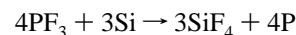
At temperatures approaching 200 °C, Pt(PF<sub>3</sub>)<sub>4</sub> loses PF<sub>3</sub> and yields a cluster, Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub>. This composition has been confirmed by Fourier transform ion cyclotron resonance mass spectrometry, but its structure is unknown. At higher temperature, the monomer yields platinum metal (confirmed by X-ray diffraction) and the expected quantity of PF<sub>3</sub> gas. The PF<sub>3</sub> produced contains no observable impurities. Ligands such as olefins do not replace the PF<sub>3</sub> in Pt(PF<sub>3</sub>)<sub>4</sub>. However, ligands like P(OCH<sub>3</sub>)<sub>3</sub> cause extensive replacement of the PF<sub>3</sub> ligand.

#### Introduction

The chemical vapor deposition (CVD) of metals such as platinum is of importance to a number of fields including electronics.<sup>1</sup> Platinum metal films are important for reasons that go far beyond chip manufacture. Pt(PF<sub>3</sub>)<sub>4</sub> is a particularly good choice as a CVD precursor for the deposition of platinum for several reasons. First, Pt(PF<sub>3</sub>)<sub>4</sub> decomposes to yield the metal at temperatures as low as 300 °C. Second, it is a stable liquid at room temperature, at which its vapor pressure approaches 40 Torr. Thus, no heating is required to make it a good precursor source. Finally, it has excellent long-term stability, unlike solid source compounds of metal complexes which must be heated to elevated temperatures for protracted periods of time.

Other sources for the deposition of platinum are being studied, particularly by Kaesz<sup>2</sup> and by Puddephatt.<sup>3</sup> They have developed various volatile organometallic source compounds. These materials are typically solids that must be heated to act as vaporization sources, but under the proper conditions, good deposits of platinum metal can be obtained.

Although the properties of Pt(PF<sub>3</sub>)<sub>4</sub> make it a good steady CVD vaporization source, its thermal decomposition chemistry is not ideal. Several studies, including our own, have found a significant phosphorus content (up to 20 atom % in some cases) in the deposited platinum films.<sup>4,5</sup> There have been no definitive studies demonstrating what chemistry is responsible for the presence of the phosphorus, although there have been several suggestions. One possibility is the reaction of PF<sub>3</sub> with platinum metal to yield PtF<sub>6</sub> and phosphorus.<sup>6</sup> Another could be the interaction of PF<sub>3</sub> with silicon<sup>2</sup> according to



We would not expect a reaction between Si and PF<sub>3</sub> (or a related reaction with SiO<sub>2</sub>) to be as clean as implied by the equation.

Our past experience with PF<sub>3</sub> shows it interacts only slowly with these kinds of potential reactants. This led to the initial idea that the Pt(PF<sub>3</sub>)<sub>4</sub> was contaminated by an impurity having volatility similar to that of the platinum compound, leading to phosphorus contamination. However, our attempts to identify such an impurity by infrared spectroscopy and by gas chromatography/mass spectrometry failed.

Most prior studies do not state whether fluorine was present as well as phosphorus in the platinum deposit. For example, PF<sub>3</sub> or some related species could be adsorbed or trapped in the platinum deposit. Zhang and Comita<sup>7</sup> deposited platinum under ultrahigh-vacuum conditions and then used mass spec-

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trometry to identify the gases given off during high-vacuum, fast-heating desorption. They found that  $\text{PF}_3$  and some  $\text{Pt}(\text{PF}_3)_x$  species are desorbed at temperatures as high as 1100 K.

We have begun a systematic study of the chemistry of  $\text{Pt}(\text{PF}_3)_4$  and other volatile metal trifluorophosphine complexes, relative to their potential as metal deposition sources. For the platinum complex in this work, a volatile yellow platinum cluster is produced at temperatures below that required for metal deposition. In this paper, we shall establish the elemental composition of that cluster, as well as several other aspects of the deposition process, including infrared and mass spectrometry of  $\text{Pt}(\text{PF}_3)_4$  itself. At this stage, it is worth noting that cluster chemistry with  $\text{PF}_3$  ligands, such as reported here, is rare, in contrast to the case of commonly observed metal clusters with carbon monoxide ligands.<sup>8–11</sup>

## Experimental Section

**Preparation of  $\text{Pt}(\text{PF}_3)_4$ .** The compound  $\text{Pt}(\text{PF}_3)_4$  was prepared by reaction of  $\text{PtCl}_2$  (Strem Chemical, Newburyport, MA) with  $\text{PF}_3$  and copper powder which had been freshly reduced by hydrogen at 400 °C.<sup>12</sup> The  $\text{PF}_3$  was in turn prepared from  $\text{SbF}_3$  and  $\text{PCl}_3$  in acetonitrile.<sup>13</sup> The platinum compound was separated from impurities by pot-to-pot distillation at  $-78$  °C followed by distillation through either  $\text{P}_4\text{O}_{10}$  or 5A molecular sieves.

The reaction of  $\text{Pt}(\text{PF}_3)_4$  with CO was carried out in a 10-cm gas cell. The infrared spectra of (a) CO at 150 Torr, (b) CO (150 Torr) and  $\text{Pt}(\text{PF}_3)_4$  (5 Torr), and (c) CO (150 Torr),  $\text{Pt}(\text{PF}_3)_4$  (5 Torr), and  $\text{PF}_3$  (5 Torr) were acquired at high resolution between 2300 and 1700  $\text{cm}^{-1}$ . The spectra were taken on either a dispersive instrument (Perkin-Elmer 983 with a model 2400 data station) or an FT-IR spectrometer (Bomem MB series). The reported results were produced by subtracting the CO spectrum from the spectra of samples b and c.

The gas evolved during the decomposition of  $\text{Pt}(\text{PF}_3)_4$  at elevated temperature was examined qualitatively by infrared spectroscopy and quantitated by *PVT* techniques. Helium was passed through a tared flask of  $\text{Pt}(\text{PF}_3)_4$ , and the mixed gas was passed through a 9 mm o.d. tube heated to 500 °C in a tube furnace. The evolved  $\text{PF}_3$  was collected in a trap at  $-196$  °C. The moles of gas were measured by *PVT* techniques by use of a vacuum system with a calibrated volume. The evolved  $\text{PF}_3$  was also examined for impurities by infrared spectroscopy in a 10-cm gas cell at several pressures.

The cluster compound,  $\text{Pt}_4(\text{PF}_3)_8$ , was prepared by passing  $\text{Pt}(\text{PF}_3)_4$  in helium through a 9-mm glass tube heated in a 12-in. tube furnace to 180–220 °C. Two strategically placed plugs of glass wool helped to improve the yield and purity of the yellow cluster compound. The first plug was placed 5 cm into the heated zone to provide a hot surface for reaction. The second plug was placed near the outlet of the heated zone; its purpose was to filter the black solid while allowing the volatile yellow solid to sublime through. The zone in which the cluster compound collected could be broken off from the remaining tubing for easy recovery.

**FT-ICR Mass Spectra.** Fourier transform ICR mass spectra were obtained from a dual-trap FTMS-2000 FT-ICR mass spectrometer (Finnigan FTMS, Madison, WI), operated at 3.0 T, equipped with CryoTorr-8 2000 L/s cryopumps (Helix Technology, Waltham, MA) for both source and analyzer vacuum chambers, with two 4.76-cm cubic traps. The cluster compound was introduced into the source vacuum chamber by means of an automated solid probe and yielded a pressure of  $(3.0\text{--}4.0) \times 10^{-8}$  Torr (uncorrected ion gauge reading) in the source chamber.

The sample vapor was ionized by an axial beam of 20 eV electrons for 20 ms at a requested emission current of 5  $\mu\text{A}$ , and ions were

allowed to partition into the analyzer trap during that period. Ions were confined by applying +1 V d.c. to each end cap electrode. Stored-waveform inverse Fourier transform (SWIFT) excitation<sup>14,15</sup> was used for all experiments, except for single-frequency excitation for collisional activation. Each time-domain ICR signal was acquired and digitized directly at a Nyquist bandwidth of 1.000 MHz to yield 128 K time-domain data. One hundred time-domain data sets were co-added and padded with an equal number of zeros prior to discrete Fourier transformation and magnitude calculation.

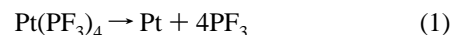
All FT-ICR spectra are unapodized except for the high-resolution mass spectrum, for which Blackman–Harris three-term apodization was employed. High-resolution data acquisition consisted of prior application of a single SWIFT waveform which included an ejection band of  $120 \leq m/z \leq 1120$  and an excitation band of  $1120 \leq m/z \leq 2000$ , in which  $m$  is ion mass in u and  $z$  is the number of elementary charges per ion ( $z = 1$  in the present examples).

Collisionally activated dissociation (CAD) spectra were acquired by prior SWIFT ejection of ions of  $190 \leq m/z \leq 1450$ . A pulse of nitrogen collision gas was then admitted into the analyzer region to a pressure of  $2.0 \times 10^{-7}$  Torr, after which the molecular ions were excited to an ICR radius of 1.5 or 2.0 cm (corresponding to 65 or 117 eV laboratory-frame kinetic energy) by resonant single-frequency dipolar excitation. The ions were allowed to collide with neutrals for 6 s before dipolar excitation/detection. At the end of each experimental event sequence, an interval of 5 s was inserted to allow the collision gas to be pumped away before the next event sequence cycle.

## Results and Discussion

Our experiments were originally designed to determine whether or not the  $\text{PF}_3$  groups in  $\text{Pt}(\text{PF}_3)_4$  are chemically altered during heating, leading to such possible fragments as  $\text{PF}_2$ ,  $\text{PF}$ , or even the phosphide ion. Also, disproportionation could yield  $\text{PF}_5$  and phosphorus. Such transformations could provide a chemical explanation for phosphorus contamination in the deposited Pt metal.

**$\text{Pt}(\text{PF}_3)_4$ .** The primary decomposition of  $\text{Pt}(\text{PF}_3)_4$  appears to follow the simple reaction



Passage of a known quantity of  $\text{Pt}(\text{PF}_3)_4$  under vacuum ( $<0.01$  Torr) through a glass tube heated to 500 °C deposits a shiny film of platinum on the walls. An X-ray diffraction spectrum of this film yields  $d$  values which match the literature pattern<sup>16</sup> for platinum to within experimental error. This observation is made for films deposited at temperatures higher than that necessary to produce crystalline platinum. However, the relative intensities of the various diffraction peaks do not match the intensity pattern for synthetic platinum, presumably because the deposit is partially textured with a nonrandom orientation of lattice planes. In three runs with 0.264, 0.359, and 0.306 g of  $\text{Pt}(\text{PF}_3)_4$ , 95, 99, and 100% of the expected quantity of  $\text{PF}_3$  was recovered, determined through liquid-nitrogen trapping of  $\text{PF}_3$  gas, followed by *PVT* techniques on a vacuum system.

The  $\text{PF}_3$  recovered from the above reactions contained no observable impurities. Neither infrared spectroscopy with a 10-cm gas cell nor GC/MS revealed significant amounts of species such as  $\text{PF}_5$ ,  $\text{POF}$ ,  $\text{SiF}_4$ , etc. In our simple CVD apparatus, the substrate is exposed to the platinum precursor vapor and its decomposition products for a very short time. The flowing gas reaction system offers a demanding stability test of  $\text{PF}_3$  with respect to side reactions or decomposition. Moreover, in several

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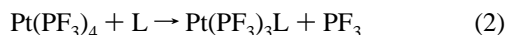
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years of working on PF<sub>3</sub> chemistry, we have never observed its disproportionation. We therefore infer that the PF<sub>3</sub> molecule maintains its integrity under a variety of conditions.

The reaction of Pt(PF<sub>3</sub>)<sub>4</sub> or its decomposition product, PF<sub>3</sub>, with glass occurs if Pt(PF<sub>3</sub>)<sub>4</sub> is heated to 500 °C in a sealed system for several hours. In that static system, etching of the glass is clearly seen, and the recovered PF<sub>3</sub> contains impurities such as SiF<sub>4</sub>, observed by infrared spectroscopy.

The nature of the platinum–phosphorus bond was probed by a series of ligand exchange experiments deriving from the general reaction



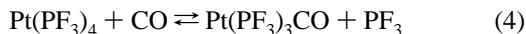
Both GC/MS and gas-phase IR indicate that simple olefins such as C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>F<sub>4</sub> do not displace PF<sub>3</sub> from Pt(PF<sub>3</sub>)<sub>4</sub> to yield monoolefin complexes in detectable quantity at room temperature and 40 Torr of both Pt(PF<sub>3</sub>)<sub>4</sub> and the olefin. Similarly, aromatic compounds such as benzene, toluene, mesitylene, and fluoroaromatics fail to displace trifluorophosphine in mixed vapor phase reactions. We conclude that equilibrium for reaction 2, with the ligands named above, must lie far to the left. In contrast, organic phosphines and phosphites readily replace PF<sub>3</sub> ligands. For example, facile exchange results from mixing Pt(PF<sub>3</sub>)<sub>4</sub> with trimethyl phosphite in a nonreacting solvent like CCl<sub>4</sub>:



The equilibrium for reaction 3 lies far to the right, since the PF<sub>3</sub> groups may effectively be titrated away by the phosphite. The composition of the product may be controlled according to the initial Pt(PF<sub>3</sub>)<sub>4</sub>:phosphite ratio. As will be reported more fully elsewhere, the individual species in solution may be identified by <sup>31</sup>P, <sup>19</sup>F, and <sup>1</sup>H NMR.

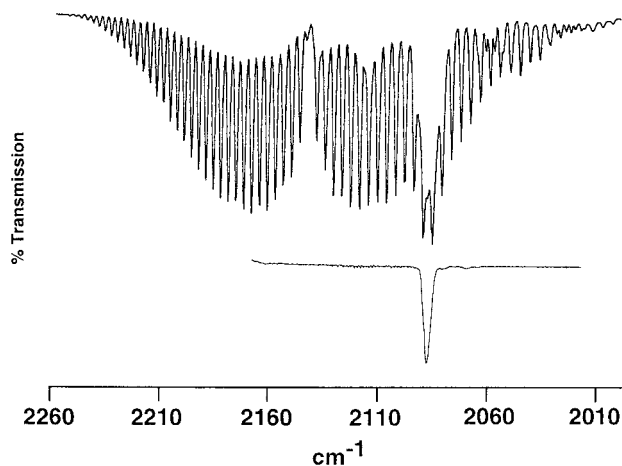
Interestingly, mixing Pt(PF<sub>3</sub>)<sub>4</sub> and carbon monoxide in the gas phase fails to produce darkening on the walls of the container flask which would characterize platinum metal formation. (Of course, Pt(CO)<sub>4</sub> has never been prepared as a stable room-temperature compound.<sup>17</sup>) However, a gas phase infrared spectrum of a mixture of Pt(PF<sub>3</sub>)<sub>4</sub> (~5 Torr) and CO (150 Torr) shows a carbonyl band distinct from the rotational fine structure of carbon monoxide. The new band is formed by the time the IR spectrum can be taken and does not change with time. Subtraction of the CO rotational fine structure from the spectrum of the mixture leaves a single carbonyl stretch at 2087 cm<sup>-1</sup> (see Figure 1, top), presumably arising from Pt(PF<sub>3</sub>)<sub>3</sub>(CO). The relative amounts of Pt(PF<sub>3</sub>)<sub>4</sub> and Pt(PF<sub>3</sub>)<sub>3</sub>(CO) may be estimated crudely as follows. The IR spectra of numerous M(PF<sub>3</sub>)<sub>x</sub>(CO)<sub>y</sub> compounds show that P–F stretching modes near 900 cm<sup>-1</sup> and carbonyl stretches near 2000 cm<sup>-1</sup> exhibit comparable molar absorptivity. Thus, since the P–F stretches we observe are vastly stronger in absorbance than the carbonyl band, we can conservatively estimate that the ratio of Pt(PF<sub>3</sub>)<sub>4</sub> to Pt(PF<sub>3</sub>)<sub>3</sub>(CO) is at least 10:1.

When PF<sub>3</sub> (5 Torr) is added to the above Pt(PF<sub>3</sub>)<sub>4</sub> and CO mixture, the monocarbonyl IR band disappears (Figure 1, bottom). These results are consistent with an equilibrium



having an equilibrium constant much less than unity.

**Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub>.** The yellow cluster mentioned above was first observed during CVD experiments in which a sealed tube



**Figure 1.** Infrared spectra. Top: CO (150 Torr) and Pt(PF<sub>3</sub>)<sub>4</sub> (5 Torr). Bottom: CO (150 Torr), Pt(PF<sub>3</sub>)<sub>4</sub> (5 Torr), and PF<sub>3</sub> (5 Torr). The IR spectrum of CO (150 Torr) alone has been subtracted from each raw spectrum to yield the displayed spectra. The regularly spaced lines are the rotational fine structure of CO, and the single band at ~2090 cm<sup>-1</sup> is Pt(PF<sub>3</sub>)<sub>3</sub>(CO).

containing Pt(PF<sub>3</sub>)<sub>4</sub> was heated to temperatures below that required for metal deposition. However, higher yields of the yellow compound were obtained from a flow system with helium or hydrogen. The carrier gas was passed through a trap containing liquid Pt(PF<sub>3</sub>)<sub>4</sub> at room temperature and then through a 9 mm o.d. glass tube heated to ~180 °C. Decomposition to a black material (presumably amorphous platinum) and a yellow solid occurred. Separation of the two compounds was aided by the use of a glass wool plug, through which the cluster would sublime. The yellow material could be handled in air for a short period but underwent considerable decomposition overnight. The yellow material was sealed in an evacuated tube and placed in a temperature gradient (70 °C maximum down to room temperature) to grow crystals by slow sublimation.

The maximum cluster yield was estimated at ~50%. The yield varied markedly according to preparative conditions: at lower temperature, most of the Pt(PF<sub>3</sub>)<sub>4</sub> was recovered unchanged; at higher temperature, the primary product was platinum metal. Interestingly, under any conditions in which the yellow cluster was produced, platinum metal was also produced. Glass wool appears to serve as a surface and filter but not as a reactant because no silicon-containing compounds were observed by infrared spectroscopy.

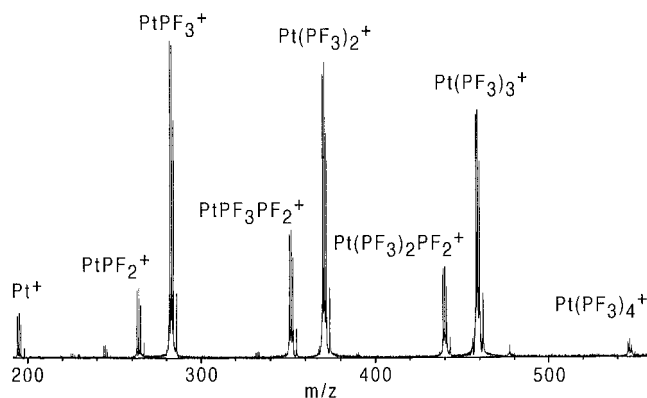
With hydrogen gas, we detected no incorporation into the material. In contrast, hydrogen is ubiquitous in lower-valent transition metal cluster chemistry.

The most definitive identification of the yellow cluster compound comes from mass spectrometry. The highest molecular weight species in the preliminary negative-ion chemical ionization mass spectrum was Pt<sub>4</sub>(PF<sub>3</sub>)<sub>7</sub><sup>-</sup>, suggesting that the parent species is Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub>, as confirmed definitively by FT-ICR MS.

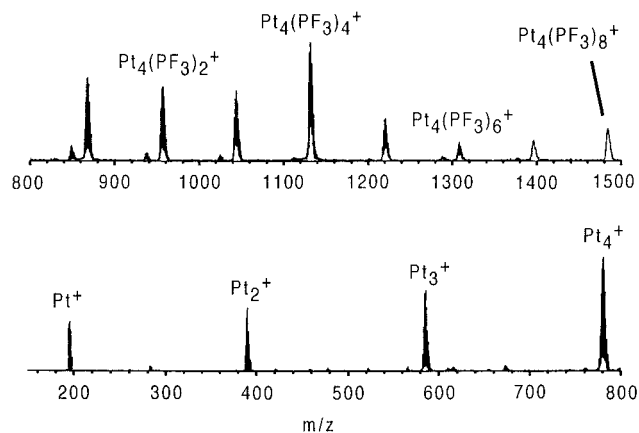
FT-ICR MS characterization began with a 20-eV electron ionization mass spectrum of the pure monomer, Pt(PF<sub>3</sub>)<sub>4</sub> (Figure 2). The low-abundance molecular ions in the range 546 ≤ *m/z* ≤ 550 include several isotopes of platinum, i.e. <sup>194</sup>Pt (33%), <sup>195</sup>Pt (34%), <sup>196</sup>Pt (25%), and <sup>198</sup>Pt (7%), whereas <sup>31</sup>P and <sup>19</sup>F are 100% abundant. The most abundant species result from sequential loss of PF<sub>3</sub> ligands, along with some additional loss of a single fluorine atom.

The broad-band electron-ionization FT-ICR mass spectrum of the yellow cluster compound (Figure 3) clearly shows the molecular ion, Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub><sup>+</sup>, as the highest-mass species, with

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**Figure 2.** Broad-band electron ionization FT-ICR mass spectrum for the monomer, tetrakis(trifluorophosphine)platinum,  $\text{Pt}(\text{PF}_3)_4$ . The molecular ion is seen, along with loss of each trifluorophosphine ligand. Minor signals correspond to the additional loss of one fluorine atom.

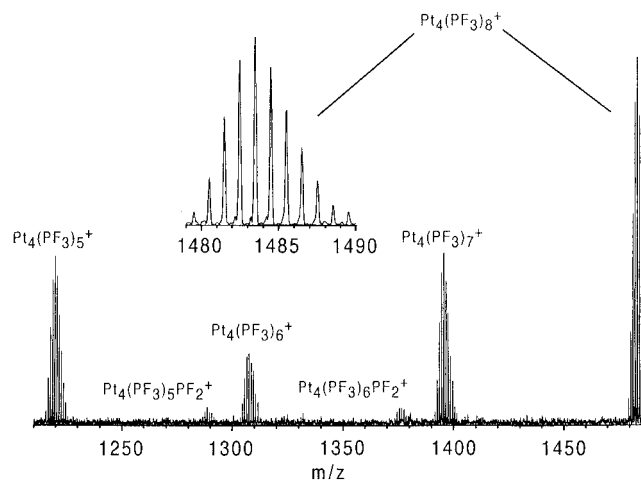


**Figure 3.** Broad-band electron ionization FT-ICR mass spectrum of the  $\text{Pt}_4(\text{PF}_3)_8$  residue produced during low-temperature chemical vapor deposition of platinum from tetrakis(trifluorophosphine)platinum,  $\text{Pt}(\text{PF}_3)_4$ . Note the fragment ions corresponding to the loss of each trifluorophosphine group from the central  $\text{Pt}_4$  core and then loss of each platinum atom.

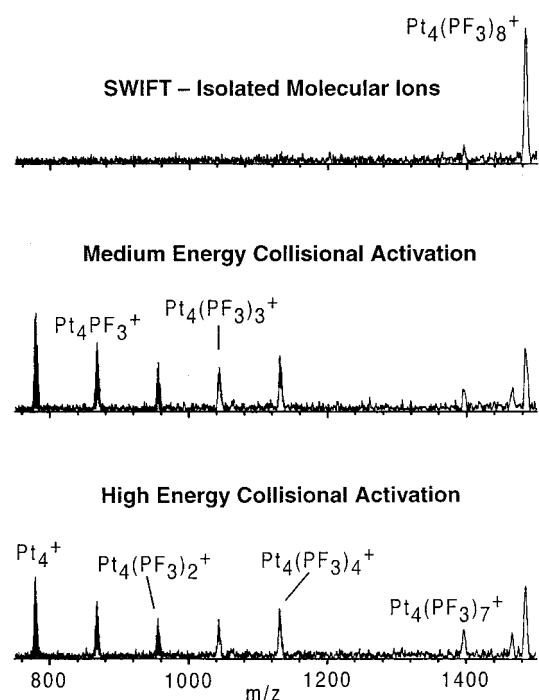
sequential losses of  $\text{PF}_3$  groups to yield ultimately the bare  $\text{Pt}_4^+$  metal cluster core, with subsequent losses of individual Pt atoms to yield ultimately  $\text{Pt}^+$ . All of the above species are clearly visible in the single broad-band mass spectrum. Essentially all ligands are lost before any Pt atoms are lost.  $\text{Pt}_4^+$  is thus independently stable, without the need for bridging groups such as  $\text{PF}_2$ ,  $\text{PF}$ , or P atoms.

The number of platinum atoms in each cluster is absolutely confirmed by high-resolution FT-ICR mass spectra (e.g., Figure 4), showing the expected isotopic abundances for a four-platinum species. Note that the isotopic abundance distribution is conserved, as expected, as successive  $\text{PF}_3$  ligands are lost.

In order to show that all of the species observed by FT-ICR MS derive from a common parent compound, we ionized  $\text{Pt}_4(\text{PF}_3)_8$  and selectively ejected ions in the range  $190 \leq m/z \leq 1450$  (i.e., all but the molecular  $\text{Pt}_4(\text{PF}_3)_8^+$  ions), by use of stored-waveform inverse Fourier transform (SWIFT) dipolar radial excitation,<sup>14,15</sup> to yield the mass spectrum of Figure 5, top. Nitrogen collision gas was then introduced to a pressure of  $\sim 2 \times 10^{-7}$  Torr, and the molecular ions were single-frequency resonantly dipole-excited to ion cyclotron radii of 1.5 and 2.0 cm (corresponding to laboratory frame kinetic energies of 66 and 117 eV) and allowed to collide with neutrals for 6 s ( $> 100$  collisions) before the final broad-band dipolar excitation/detection. (An additional delay of 5 s after detection allowed for the collision gas to be pumped away before the next repetition of the experimental event sequence.) The



**Figure 4.** High-resolution electron ionization FT-ICR mass spectrum obtained by ejecting all ions below  $m/z$  1200 and narrowing the detection bandwidth by a factor of 10. The isotopic distribution and the exact masses match closely to those of  $\text{Pt}_4(\text{PF}_3)_8^+$ .



**Figure 5.** FT-ICR mass spectra following collisional activation of the molecular ion (including all isotopes) with dinitrogen, to yield  $\text{Pt}_4(\text{PF}_3)_n^+$ ,  $n = 0 - 4$ .

appearance of the various  $\text{Pt}_4(\text{PF}_3)_x^+$  fragment ions confirms that they derive from the  $\text{Pt}_4(\text{PF}_3)_8^+$  parent ions. In other words, the FT-ICR mass spectra can all be explained by the presence of a single  $\text{Pt}_4(\text{PF}_3)_8$  parent compound.

**Other Evidence.** Little is known about  $\text{PF}_3$  polynuclear or cluster chemistry.<sup>8-11</sup> We were especially concerned about species analogous to  $(\text{PF}_3)_3\text{Fe}(\text{PF}_2)_2\text{Fe}(\text{PF}_3)_3$ <sup>18,19</sup> and  $\text{Ir}_3\text{P}(\text{PF}_3)_9$ <sup>20</sup> relative to the issue of phosphorus contamination. However, no mass spectral traces of such species were seen in the chemistry of  $\text{Pt}(\text{PF}_3)_4$  and  $\text{Pt}_4(\text{PF}_3)_8$  or from the conversion of one to the other.

Unfortunately, X-ray crystallography has so far proved incapable of yielding a molecular structure for  $\text{Pt}_4(\text{PF}_3)_8$ . Microscopically good-looking crystals fail to yield any diffrac-

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tion spots on a random search pattern as one attempts to index the crystal. Two efforts to obtain data sets at low temperature also failed. Although it seems reasonable to assume that each molecule in the lattice is fairly symmetric, the presence of fluorine atoms on the molecular periphery may permit extensive motion of molecules within the unit cell.

Infrared spectroscopy confirms that P–F bonds (and no other functional groups) are present but does not rule out the possibility of PF<sub>2</sub>. In this respect, the FT-ICR mass spectra definitively establish the presence of PF<sub>3</sub> (and not PF<sub>2</sub>) groups.

NMR offers some additional information. The <sup>31</sup>P and <sup>19</sup>F NMR spectra of both Pt(PF<sub>3</sub>)<sub>4</sub> and Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> are readily seen even with small amounts of material. Both nuclei in both compounds yield fairly broad, complex, mirror-imaged patterns. The broadness and complexity are caused by the chemical equivalence, but magnetic inequivalence, of the PF<sub>3</sub> groups. This yields a very complex second-order pattern that results from many overlapping lines. The fluorine pattern of both compounds is a basic doublet caused by a coupling of about ~1300 Hz to the phosphorus atom. This doublet is partially split into a further doublet owing to the 34% abundance of spin 1/2 <sup>195</sup>Pt. The phosphorus spectrum is a basic quartet with the same ~1300 Hz coupling to the fluorine atoms again further coupled to the platinum. The platinum coupling to phosphorus is ~6550 Hz, and that to fluorine is ~415 Hz. The true phosphorus–fluorine coupling constants are close, but not exactly the frequency difference between the major spikes in the fluorine or phosphorus spectra. If the PF<sub>3</sub> groups are not chemically equivalent, the mirror-imaged symmetry around the center frequency will be broken. There is no sign of anything other than a mirror pattern for either compound. The compound Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> shows a downfield chemical shift from Pt(PF<sub>3</sub>)<sub>4</sub> of 63.9 ppm in the phosphorus spectrum and a 9.92 ppm upfield shift in the fluorine spectrum. The breadth of the pattern of lines is comparable to the patterns we generally see when there are three or more equivalent PF<sub>3</sub> groups present in a compound. In these circumstances, there are so many overlapping lines that substructure beyond that described above is rarely seen. However, the patterns do not have any of the characteristics (yet further broadening) that we have seen for fluxional compounds in the coalescence region.

Limited fluorine and phosphorus NMR studies of these compounds were made by examining one nucleus while the other nucleus was decoupled. This simplified the spectra to single lines with only the platinum coupling remaining. The much sharpened patterns further confirm the presence of only one type of PF<sub>3</sub> group.

NMR mitigates against the presence of features like PF<sub>2</sub> groups as does FT-ICR. The apparent equivalence of the PF<sub>3</sub> groups implies a tetrahedral structure for the Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> compound. However, the strong possibility of fluxional behavior makes it uncertain that the compound is as symmetric (e.g., *T<sub>d</sub>* symmetry) as implied.

Platinum NMR should eliminate most, if not all, of the second-order coupling caused by magnetic inequivalence and yield more accurate coupling constants. For Pt(PF<sub>3</sub>)<sub>4</sub>, it does.

A beautiful first-order platinum-195 spectrum was obtained, having a quintet from phosphorus coupling (*J* = 6500 Hz). The components of the quintet were further split, and most of the lines of a 13-line multiplet for fluorine coupling (*J* = 416 Hz) were seen. In spite of considerable effort, a platinum spectrum of Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> could not be seen. We tried a run ~40 °C higher in temperature in case coalescence broadening occurs at room temperature.

In future reports, we will discuss further reactions of the monomer and cluster with various ligands. However, it should be reported here that Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> reacts with PF<sub>3</sub> slowly to regenerate the monomer Pt(PF<sub>3</sub>)<sub>4</sub>. This reaction proceeds with the neat compound and PF<sub>3</sub> under slight pressure. The presence of the monomer was confirmed by both IR and GC/MS. This reaction further suggests that there is a simple equilibrium between the monomer and the cluster.

## Conclusion

The preparation of a stable platinum cluster, Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub>, is unexpected. Up to this stage, few polynuclear PF<sub>3</sub> complexes have been seen, and most have been partially substituted carbonyl compounds. For example, in preparation of Ru<sub>3</sub>(PF<sub>3</sub>)<sub>x</sub>(CO)<sub>12-x</sub>,<sup>21</sup> *x* can become as large as about 6 before the trimer breaks up to form the monomer. There are also several excellent examples of trifluorophosphine-containing clusters of heteronuclear cobalt and rhodium or iridium carbonyls.<sup>22</sup>

The electron count in the Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> neutral cluster is 56, which is also unusual. Typically, with an electron count of 60, the metal core will be tetrahedral, with 62 and 64 for the butterfly and square-planar structures, respectively. With fewer than 60 electrons, the structure is often tetrahedral with multiple metal–metal bonding in the core.

It is tempting to conclude that the size of the trifluorophosphine group limits the maximum number of ligands. Molecular mechanics calculations will probably be required to prove this supposition.

Finally, we see nothing in the cluster chemistry that yields a simple explanation for the phosphorus content in a platinum deposit. We are currently studying the variables of the CVD process more carefully as well as the chemistry of the cluster compound.

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**Supporting Information Available:** Phosphorus and fluorine NMR spectra, with and without decoupling, for Pt(PF<sub>3</sub>)<sub>4</sub> and Pt<sub>4</sub>(PF<sub>3</sub>)<sub>8</sub> (9 pages). Ordering information is given on any current masthead page.

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